

Effect of surface acoustic waves on the catalytic decomposition of ethanol employing a comb transducer for ultrasonic generation

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Abstract

The effect of surface acoustic waves, generated on a silver catalyst using a comb transducer, on the catalytic decomposition of ethanol is examined. The comb transducer employs purely mechanical means for surface acoustic wave (SAW) transduction. Unlike interdigital SAW transducers on piezoelectric substrates, the complicating effects of heat generation due to electromechanical coupling, high electric fields between adjacent electrodes, and acoustoelectric currents are avoided. The ethanol decomposition reactions are carried out at 473 K. The rates of acetaldehyde and ethylene production are retarded when acoustic waves are applied. The rates recover to varying degrees when acoustic excitation ceases.

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Keywords: Surface acoustic waves (SAW); Heterogeneous catalysis; Comb transducer; Ethanol decomposition

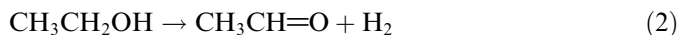
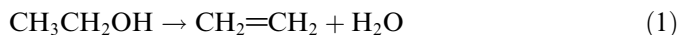
1. Introduction

Traditional sonochemistry, which uses ultrasound to produce cavitation in liquids, has been used for some time to enhance and study homogeneous catalysis [1,2]. Cavitation injects large amounts of thermal energy into a liquid through the implosion of gas bubbles [3]. In homogeneous catalysis, this influx of energy is the driving force behind the catalytic effect of ultrasound. In heterogeneous catalysis, the relevant physiochemical processes occur at, or near, a solid/fluid interface. The ultrasonic energy in a surface acoustic wave (SAW) is strongly confined to the solid/fluid interface [4]. Therefore, SAWs are ideally suited to study the effect of transient strains and surface motion on heterogeneous catalysis. The surface specific character of SAWs has been previously exploited to artificially control ethanol decomposition on a thin Cu film catalyst [5] and to study adsorptive properties of thin ZnO and NiO films [6].

Realization of SAWs as an efficient and flexible technique for probing and controlling the physical processes involved in heterogeneous catalysis requires addressing a number of experimental concerns. The experimental techniques implemented to date require lithographic fabrication of an interdigital SAW transducer and subsequent coating of the test section of the piezoelectric substrate with a thin catalyst. This method of sample preparation is expensive and time consuming. Furthermore, isolation of the relevant physiochemical processes is complicated by heating due to electromechanical coupling losses associated with acoustic generation [7], the presence of electric fields between adjacent electrodes, and acoustoelectric fields [8–10].

As an alternative, we investigate the efficacy of a comb transducer for insonifying a catalyst. The SAWs are induced mechanically with no electric field present, and although heat energy is imparted through thermo-elastic coupling, the quantity is negligible and can be ignored [11]. The process investigated is catalytic ethanol decomposition on a silver catalyst [12]. The process reactions are dehydration—to produce ethylene (Eq. (1)), and dehydrogenation—to produce acetaldehyde (Eq. (2)).

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These reactions are selected because they are relatively simple, allow catalyst activity and product selectivity to be evaluated, and the effects of SAWs on the reactions have been investigated previously with the aid of interdigital acoustic transducers. Our results demonstrate that SAWs generated using a comb transducer do affect the catalytic activity of a silver film. Specifically, for the temperature and reactant concentrations investigated, SAWs retard the rates of ethylene and acetaldehyde formation.

2. Experimental set-up

To evaluate the effect of surface acoustic waves on the catalytic action of a silver catalyst, a low pressure gas recirculation reactor is constructed. Reactant and product concentrations are determined off-line using gas chromatography. Silver catalyst samples are prepared by vapor deposition of ~ 30 nm silver films on stainless steel substrates. Surface acoustic waves are generated using a comb transducer [13,14]. To simplify the design and avoid excessive acoustic losses due to acoustic impedance mismatch, the comb was machined into the end of a thermal barrier stand-off and coupled to the catalytic surface using a high temperature acoustic couplant. A 1 MHz piezoelectric transducer is used to excite longitudinal waves that propagate down the shaft of the stand-off (Fig. 1). Teeth, having a spacing equal to the Rayleigh wavelength (λ_R) at 1 MHz, machined into the sample end of the stand-off serve to resonantly excite Rayleigh waves that propagate along the sample surface [15].

A stainless steel reaction cell (with a quartz glass window for laser diagnostic access) houses the silver catalyst on its stainless steel substrate (see Fig. 1). The substrate

has a machined cavity that snugly accommodates a cartridge heater. A thermocouple fits into a small cavity opposite the heater and is used for feedback temperature control. The chamber is evacuated to less than 0.1 Torr and the catalyst is heated to 473 K. Ethanol and oxygen are injected into the evacuated reaction cell. Reactants are circulated over the catalyst surface via a closed recirculation loop driven by a bellows type vacuum pump. The recirculation loop includes a 1 L reservoir to ensure that the gas samples extracted do not substantially deplete the volume of reactants and products in the reaction cell. 1 mL gas samples are extracted at 15 min intervals and fed into a gas chromatograph/flame ionization detector (GC/FID) for analysis. Acetaldehyde and ethylene production rates are measured and normalized against the quantity of ethanol present in the sample. A photorefractive interferometer [16] is employed to monitor the out-of-plane surface displacements (~ 2 nm) associated with SAW propagation along the catalyst surface [17].

3. Results

Surface acoustic waves depress the rate of acetaldehyde and ethylene production to varying degrees. Tests were conducted over a range of reactant concentrations, in some cases re-using catalyst coatings. Activity of the catalyst samples is found to vary significantly from one sample preparation to another. Reactant ratios tested range from $\approx 4:1$ to $1:3$ ($\text{C}_2\text{H}_5\text{OH}:\text{O}_2$). Tests employing a freshly prepared catalyst and a $1:1$ ratio of ethanol to oxygen yield the most definitive results. Fig. 2 depicts results under these conditions. When the catalyst is insonified with SAWs, the reaction rate is retarded. When the SAWs cease, the reaction rate recovers.

The relative concentrations of acetaldehyde and ethylene as a function of time are shown in the upper and lower

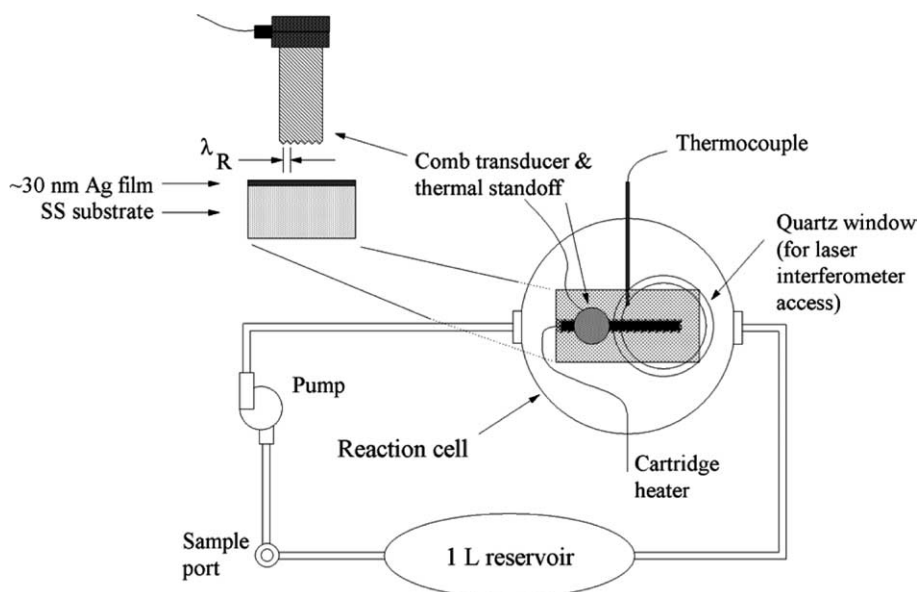


Fig. 1. Schematic of experimental apparatus including details of the catalyst film and comb transducer.

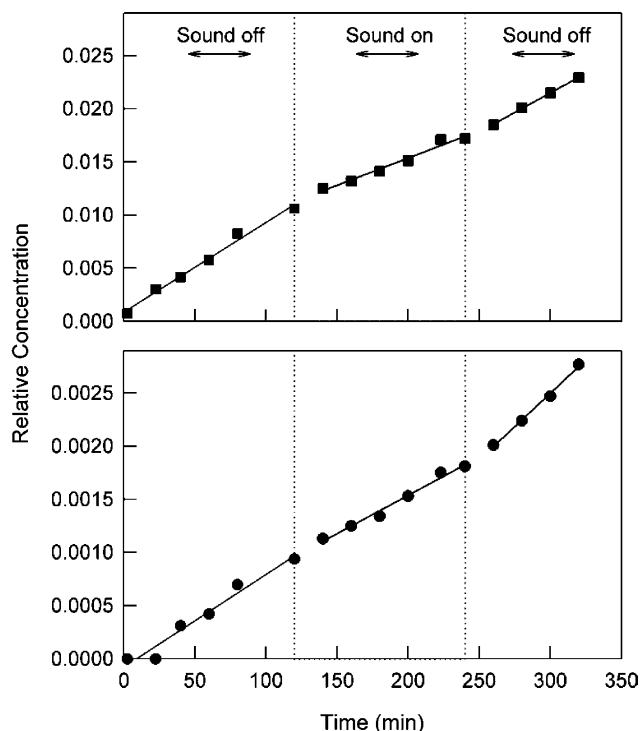


Fig. 2. Relative concentration versus time for acetaldehyde (■) and ethylene (●). The rates of formation of both products decrease in the presence of SAWs. Subsequently, the rates recover when insonification ceases.

panes, respectively, of Fig. 2. Initial concentrations of ethanol and oxygen are 34 and 40 Torr, respectively. The ethylene formation rate is an order of magnitude lower than the acetaldehyde formation rate. Initially, the reactions occur devoid of ultrasonic influence. After 120 min the sample is insonified with SAWs, and the reaction monitored for the next 120 min. While insonified, the relative rate of acetaldehyde formation decreases to 61% of the initial rate. Upon turning the sound off at 240 min, the rate of acetaldehyde formation recovers to 87% of the initial rate. When insonified at 120 min, the relative rate of ethylene formation decreases to 83% of the initial rate. Upon turning the sound off at 240 min, the rate of ethylene formation recovers to 144% of the initial rate.

Incomplete recovery of the acetaldehyde formation rate may be due to the formation of oxides on the catalytic surface [18] or fouling of the catalytic surface by constituents in the acoustic couplant. Recovery of the ethylene formation rate to greater than its original value may be due to a cleansing effect. The catalytic surface is refreshed or cleaned by the SAWs [9].

3.1. Experimental controls

Many variable parameters are present in these tests which may conceal the effect of SAWs. To delineate the direct consequence of the SAWs acting on the silver catalyst from other potential camouflaging effects, such as decomposition of the couplant, control tests are conducted.

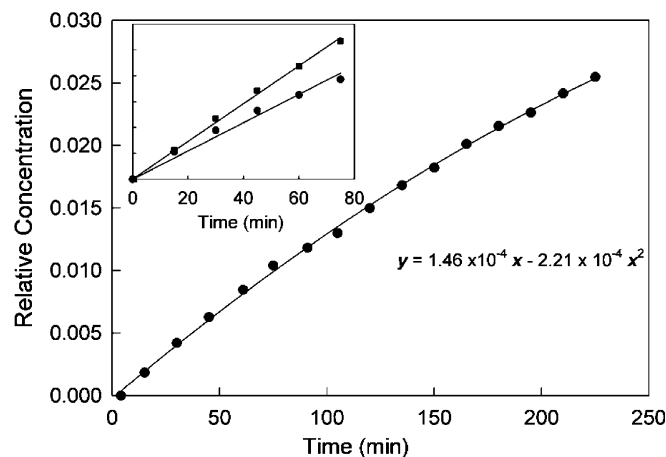


Fig. 3. Relative concentration versus time for acetaldehyde produced with no acoustic couplant present in the reaction cell. The reaction rate decreases in time, despite the absence of the couplant. Inset: Relative concentration versus time for acetaldehyde produced with a silver catalyst (■) and a stainless steel catalyst (●).

The first test involves using the same experimental parameters as those used in the test depicted in Fig. 2, but with no acoustic couplant (and thus no SAWs) applied to the sample surface [19]. The rate of acetaldehyde production is comparable to other tests during periods when no acoustic waves are present, suggesting that decomposition of the couplant either does not occur or does not produce constituents that interfere with ethanol decomposition. However, the overall reaction rate decreases with time, as demonstrated by the quadratic fit to the data (see Fig. 3). This observation suggests that, over time, the reaction is inhibited by the formation of oxides on the catalytic surface [18]. Moreover, this data suggests oxide formation, not couplant fouling, explains the incomplete recovery of the acetaldehyde formation rate in Fig. 2.

A second baseline test examines the reaction rate in the absence of a catalyst. A test is run using the stainless steel substrate with no silver coating. The rate of acetaldehyde production is significant but lower than when a silver catalyst is present. See the inset in Fig. 3. The fact that acetaldehyde is produced in the absence of silver suggests that, at 473 K, stainless steel acts as a catalyst for ethanol decomposition.

In general, the results of the experimental control tests suggest two mechanisms, apart from SAW catalysis, are at work in these experiments. One, the temporal decline in reaction rate is due to the oxidation of the catalyst surface. Two, at 473 K, stainless steel—to a lesser degree than silver—acts as a catalyst in ethanol decomposition, providing a secondary catalytic surface which dilutes the impact of insonification of the silver catalyst.

4. Discussion

Our results show that SAWs decrease the ethanol decomposition rate. The temperature at which the experiments are carried out potentially favors an oxide phase

on the catalyst surface. Oxidation of the silver surface likely retards the reaction rate. In a similar experiment employing a copper catalyst, Inoue and Matsukawa [18] show SAWs retard ethanol decomposition on a copper catalyst at 403 K, while SAWs enhance the reaction at temperatures below 393 K. They attribute the effect at 403 K to oxidation of the copper surface. In complementary work, Watanabe et al. [20], employing X-ray photoelectron spectroscopy, shows that a metallic silver catalyst is converted to an oxide state in an ethanol decomposition reaction at 473 K. Further, they reinforce this argument based upon the similarity between their results and previous results employing oxide catalysts.

The mechanism responsible for the shift—either up or down—in the reaction rate is the source of current debate. It has been shown that acoustic waves induce transient strains and surface motion that preferentially favor or disfavor the reaction. However, the transient strain associated with propagation of SAWs ($\sim 10^{-6}$) is well below the threshold of activation for surface chemical processes ($\sim 10^{-3}$) [9,21]. Furthermore, thermal SAW mechanisms can be neglected. In our experiments, heat generated due to electromechanical losses in the piezoelectric transducer is thermally isolated from the substrate with a thermal stand-off, and the propagation of linear, elastic SAWs (in the MHz range) along the substrate surface generate negligible thermal energy [11]. An alternative explanation involves SAWs influencing the spatial distribution of adsorbates. Zaera et al. [22] has shown that the overall reaction rate of various heterogeneous catalytic systems strongly depends on the spatial distribution (random versus clustered arrangements) of oxygen atoms on the catalyst surface. The supposition here is that localized strains associated with SAW propagation affect the spatial distribution of adsorbates and hence the overall reaction rate [23].

5. Conclusion

Surface acoustic wave catalysis is demonstrated on a well-known catalytic reaction—decomposition of ethanol on a silver catalyst. A comb transducer is employed for ultrasonic generation. This work complements and contrasts previous studies involving interdigital SAW transducers on piezoelectric substrates. Employing a comb

transducer, SAWs are generated by purely mechanical means. Mechanical generation avoids the complicating effects of heat generation due to electromechanical coupling, high electric fields between adjacent digits, and acoustoelectric currents. Our results show that, for the temperature and reactant concentrations investigated, SAWs retard ethylene and acetaldehyde formation rates.

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